

DETECTING OCEAN CURRENTS BY OBSERVING THEIR HYDROGEN-ION CONCENTRATION.

By ALFRED GOLDSBOROUGH MAYOR.

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OBSERVATIONS.

The surface water of the middle regions of the Tropical Pacific commonly flows in a westerly direction due to the effect of the trade winds, and this water is strongly alkaline, its hydrogen-ion concentration being about 8.22 PH, or 0.602×10^{-8} . Occasionally, however, in the Tropical Pacific one finds a region wherein the surface water is temporarily flowing toward the east and thus counter to the trend of the usual current and of the trade winds. I find that this easterly moving water is commonly less alkaline than is that of the general region in which it occurs. Thus while the water moving toward the west is about 8.22 PH these easterly counter currents are 8.1 to 8.18 PH, or 0.83×10^{-8} to 0.66×10^{-8} .

The tension of the carbon dioxide of the great westerly current appears to about the same as that of the air above the sea ranging in our tests from 2.75 to 3.25 ten thousandths of an atmosphere, whereas the water which is moving in an easterly direction is more strongly changed with free CO_2 , its tension ranging from 3.45 to above four ten thousandths of an atmosphere. Moreover, this easterly moving water is slightly colder than that of the general region in which it occurs and Professor L. R. Cary found its oxygen content was higher than normal. Thus it seems that these counter currents are caused by deep water which has temporarily appeared upon the surface either by welling upward or through a local displacement of the westerly-moving surface layer.

This suggests that eddies may be set up due to the gusty nature of the trade winds, as shown in Fig. 1. Every "puff" pushes some water ahead of it and leaves a hollow in its wake which must be filled up to the general level by deeper water rising to the surface,

and this deeper water is in turn replaced by the water which has been temporarily heaped up in front of the gust. There is nothing to prevent an under-water counter current, whereas in order to fill the hollow by surface water the current would have to move against the prevailing wind as at *a*, Fig. 1; and the friction between air and

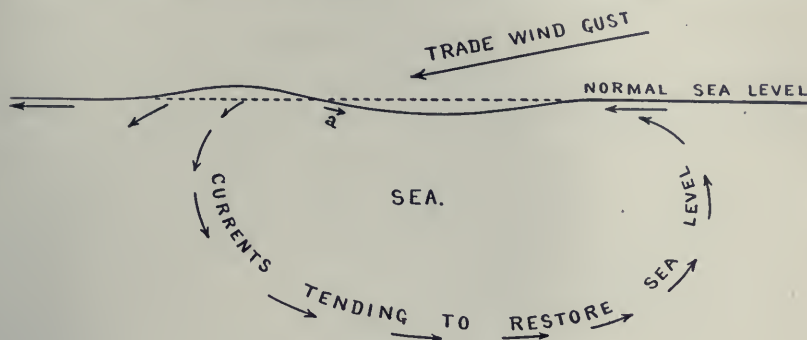


FIG. 1.

water is much greater than that between water particle and water particle. Despite this process of local adjustment, however, the westerly trend of the surface current tends to raise the general ocean level in the western regions of the Tropical Atlantic and Pacific, and this is counterbalanced by the great oceanic surface eddies of which the Gulf Stream and the Japan Current are well known examples. The general up-welling of deep water in tropical regions has been known since the cruise of the *Challenger*.

Thus due to local causes, water from the depths of the Tropical Pacific sometimes comes to the surface in large quantity, and retains some of its easterly movement, even against the prevailing wind. Then upon being heated by the sun and mixing with the warm surface waters its capacity for retaining free CO_2 is reduced, and its carbon dioxide passes out into the atmosphere.

As is well known McEwen, 1910, 1916, etc., has demonstrated from studies of salinity that great quantities of deep water are constantly welling up along the Pacific coast of America, and in confirmation of this fact I find that the CO_2 tension of the surface water along the Pacific coast of the United States is considerably higher than we would expect from its low temperature, and much

above that of the water farther off the coast. Thus a PH of 7.85 at 10.5° C., and CO₂ tension of 5.4 ten thousandths of an atmosphere were observed 54 miles off Golden Gate, San Francisco, on May 1, 1917; and somewhat similar conditions were seen off Vancouver in September, 1918.

An up-welling of deep water due to off shore winds has also been demonstrated by Bigelow, 1917, p. 241; along the coast of New England north of Cape Cod, but this effect is neither so marked nor so constant in the shallow water along our Atlantic seaboard as it is off the abrupt slope of the Pacific coast. Indeed Bigelow, 1915, 1917, has shown that the cold water which drifts down the Atlantic coast from Nova Scotia to Florida is chiefly derived from the Gulf of St. Lawrence and receives accessions from surface drainage and from rivers along its whole course.

McClendon, 1917, 1918, showed that the CO₂ tension of surface water at Tortugas and in the Gulf Stream, is on the average about in balance with the atmosphere, 30 determination indicating that the pressure of carbon dioxide of the air ranges from 2.8 to 3.5 ten-thousandths of an atmosphere, while that of the surface water of the Tortugas lagoon on the east side of Loggerhead Key ranged from 2.6 to 3.5 ten-thousandths of an atmosphere, and that of the Gulf Stream from Key West to Cape Hatteras was from 3.2 to 3.5. McClendon also found that photosynthesis by marine plants in sunlight is a very important factor in controlling the hydrogen-ion concentration of the water of shallow lagoons or tide pools where the bottom is covered with sea weed; for the plants reduce the CO₂, thus setting free oxygen and causing the water to become highly alkaline. For example, while the PH of the sea around the Tortugas is about 8.22 that of the lagoon rose at times to 8.35 by day and sank to 8.18 at night, and the hot shallow lagoon of the Marquesas, Florida, had a PH of 8.46 accompanied by precipitation of calcium carbonate. McClendon was, however, unable to find any appreciable diurnal range in hydrogen-ion concentration of the surface water in the open sea nor can I detect it from my studies in the Atlantic and Pacific.

Also Wells, 1918, p. 6, shows that the water of the Gulf of Mexico contains about 0.092 grams of CO₂ per liter and its surface

tension is thus in balance with the atmosphere, and I find that when uninfluenced by up-welling of unusual quantities of deep water the CO_2 tension of the surface waters of the Tropical Atlantic and Pacific is also practically in balance with the atmosphere.

Thus on the voyage of the S. S. *Niagara* from Fiji to Honolulu, September 6 to 12, 1918, we encountered only the prevailing westerly set uninterrupted by any currents moving toward the east, and the average PH was about 8.22, the average temperature 28°C ., and the CO_2 tension of the water three ten-thousandths of an atmosphere and thus practically the same as that of the air. When cold deep water wells upward to the surface, however, a different condition ensues, for due to relief of pressure and increase in temperature this water must discharge its excess CO_2 into the atmosphere.

Thus on the voyage of the S. S. *Sonoma* between Honolulu and Pago Pago, Samoa, June 25 to 30, 1918, we at times met with strong currents set toward the east and the average PH was about 8.19 and the CO_2 tension of the surface water 3.26, the average temperature being 28°C ., as on the voyage of the *Niagara*. Similarly on the voyage of the S. S. *Ventura* from Pago Pago, Samoa, to Honolulu on April 19 to 25, 1917, we met with several strong sets to the eastward and the average PH was 8.17, the CO_2 tension 3.35 and the temperature 25.7°C .

Henderson and Cohn, 1916, p. 621, conclude from laboratory experiments that upon the whole in most places and at most seasons carbon dioxide must be escaping from the sea into the air, although they also state that the balance is doubtless restored by CO_2 entering the water from the air in the polar regions. These authors did not consider the effect of photosynthesis by marine plants which McClendon afterward showed to be such an important factor. Were it not for photosynthesis it is probable that large quantities of carbon dioxide would escape from the sea in the tropics, but instead of this McClendon, Wells and I find that the warm waters are practically in balance with the atmosphere.

My observations along the Atlantic coast between Nova Scotia and Florida in December–March show also that the coastal current during these cold months has a CO_2 tension somewhat below that of the atmosphere, and this may be due to the great concentration of plant life in these cold waters.

Thus according to my observations the averages for the shore current the salinity of which ranges from 30 to 33 grams in 1,000 grams of water, between Nova Scotia and northern Florida in winter are: Temperature 6.7° C., salinity 31.7, PH 8.05 and CO_2 tension 2.5 ten-thousandths of an atmosphere, while similar data for the Gulf Stream of salinity 36 at the same season between the Straits of Florida and Cape Hatteras are: Temperature 22.3° C., salinity 36.35, PH 8.21, and CO_2 tension 2.77. Thus the cold shore water seems to be in a condition to absorb CO_2 from the air, while the warm Gulf Stream waters are more nearly in balance with the atmosphere. In summer when the shore current is warmed to about 22° C., its CO_2 tension rises to be quite in balance with the atmosphere, as is indicated by McClendon's Table VII., p. 226, 1918.

It is well known from the extensive work of Blackman and Smith that photosynthesis about doubles in effect for 10° C. rise in temperature, but due to the action of denitrifying organisms such as Drew's *Pseudomonas calcis* the tropical waters are deprived of nitrogen and can thus support only a meager plant life in comparison with that of colder regions. Thus McClendon found less than 0.01 mg., of nitrogen per liter as nitrates and nitrites at Tortugas, Florida, while Raben, 1910, found more than ten times these amounts in the North Sea; and as shown by McClendon the tropical ocean despite its high temperature can only eliminate a small part of its free CO_2 by photosynthesis due to the scarcity of plant life.

Krog, 1904, calculated that if the average CO_2 tension of the ocean is the same as that of the air (about 0.0003 atmosphere), it must contain twenty-seven times as much CO_2 as the air. Thus if the ocean gave off one tenth of its CO_2 to the air the carbon dioxide tension of the sea would sink to 0.0002 atmosphere. He found that the CO_2 in the air of Disko Island, Greenland, ranged from 0.00025 to 0.007, being high with winds from the north and west, and low when the wind blew from the south and east. The turbid sea water at Disko Island had a CO_2 tension of 0.0001 to 0.00035, while the clear water in the same region had a tension of 0.00035 to 0.0006 atmospheres, thus apparently being lower than that of the surrounding air.

Also the CO_2 tension of the surface water between Cape Fare-

well, southern Greenland and the Shetland Islands was distinctly lower than that of the air.

The average CO_2 tension of the air over the ocean seems to be about 0.000295, this being the mean of 51 observations made by Thorpe between Brazil and England. In 1917, however, using apparatus given to me by Professor McClendon, I tested the CO_2 tension of the air over the Pacific between Samoa and San Francisco, but there was apparently no relation between the local CO_2 tension of the air and that of the water under the air, this lack of coördination being due in all probability to the great mobility and rapid fluctuation in CO_2 tension in the air as compared with that of the water. It would apparently be necessary to obtain several thousand determinations of the CO_2 tension of air over the ocean taken at all seasons and in all weathers to determine its mean CO_2 tension with accuracy, but the determinations that have been made indicate that it is not far different from that of the air over the land. My average for three voyages over the Tropical Pacific is: Temperature 27.5° , PH 8.22, and CO_2 tension 3.15 ten thousandths of an atmosphere. Thus the tropical waters appear to have a CO_2 tension slightly above that of the atmosphere.

We lack sufficient data for a definite statement as to whether CO_2 is on the whole passing from air to sea or *vice versa*, but the surmise may seem reasonable that a balance is maintained; the absorption of CO_2 from the air by the Polar Seas being offset by its passing out of the ocean over the wide area of the tropics, while the temperate regions stand in an intermediate relation, the water absorbing CO_2 during the winter and giving it out to the air during the summer.

It may be of interest to compare our observations with those of Palitzsch, 1911, who was the first to apply Sørensen's colorimetric methods to the study of the hydrogen-ion concentration of sea water.

Palitzsch used naphtholphthalein and phenolphthalein as indicators and tested the PH of the Black Sea, Sea of Marmora, Mediterranean, Atlantic and North Sea in summer with the following results:

Locality.	PH of Sea Water.
Black Sea { surface	8.34
{ deep water	7.45
Sea of Marmora and Bosphorus	8.35
Eastern Mediterranean	8.27
Western Mediterranean	8.22
Coast of Portugal	8.25
Off Scotland and Faroe Is.	8.08-8.22
S.E. part of North Sea and Skagerak	8. -8.05

METHODS.

The hydrogen-ion concentration of sea water was tested by the simple process of placing 0.4 c.c. of $\frac{1}{10}$ of 1 per cent. thymolsulphophthalein in a non-soluble glass test tube of 24 mm. caliber and adding 30 c.c. of the sea water to be tested. Highly alkaline sea water gives a blue-green solution, while relatively acid water gives a greenish-yellow color. Then by comparing this test tube with a series of sealed tubes of similar caliber containing mixtures of borax, boracic acid and sodium chloride of various known hydrogen-ion concentrations we can at once determine the concentration of our sample sea water with an error of not more than 0.025 PH.

McClendon, Gault and Mulholland, 1917, were the first to standardize sodium borate and boracic acid mixtures for use in measuring the hydrogen-ion concentration of sea water with thymolsulphophthalein as an indicator. Their solution consists of 0.075 m. sodium borate (28.67 grams of $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$), and 19 grams of sodium chloride, dissolved in water so as to make up 1,000 c.c. of solution. The other solution consists of 0.3 m. boric acid (18.6 grams of H_3BO_3) and 22.5 grams of sodium chloride dissolved in water so as to make up a liter of solution. Definite mixtures of these two solutions give correspondingly definite hydrogen-ion concentration, as is shown by McClendon, Gault and Mulholland, p. 44, 1917.

Professor McClendon kindly gave me a set of these tubes which I have used on voyages to test the hydrogen-ion concentration of the surface water of the ocean. The readings of these tubes were compared with those of a Leeds and Northrup potentiometer standardized by the U. S. Bureau of Standards. McClendon thus tested their accuracy in 1917 and I repeated the process in April, 1919,

and found that the colors of the tubes, which had been carefully guarded from light when not in use, had not change in the interval.

As is well known the unit of hydrogen-ion concentration is 1 normal hydrogen-ion per liter of water, or about 1 gram of hydrogen-ion per liter. The purest distilled water contains only about 1 gram of hydrogen-ion in 10,000,000 liters of water at about 22° C., and thus its hydrogen-ion concentration is about 10^{-7} . Sea water, however, is alkaline and contains only about one tenth this concentration of hydrogen-ions, or as we say its hydrogen-ion concentration is about 10^{-8} .

In order to avoid writing negative exponents Sørensen, 1909, p. 28, devised the symbol "PH" to indicate the negative logarithm of the hydrogen-ion concentration. Thus according to Sørensen's system a normal hydrogen-ion concentration, or 10^0 of H-ions per liter, is written PH 0; a decinormal H-ion concentration, or 10^{-1} , is PH 1; while sea water with somewhat less than 0.000,000,01 normal hydrogen-ion concentration is about 10^{-8} normal and is designated 8 PH.

If for example a specimen of sea water had a hydrogen-ion concentration of

$$\frac{1}{1.622 \times 10^8} = 0.616 \times 10^{-8},$$

we would call its PH 8.21 because 0.21 is the logarithm of 1.622, and 8 is the logarithm of 10^8 and $0.21 + 8 = 8.21$.

McClendon's borax-boracic colorimetric tubes indicate the true PH of sea water containing 32 to 33 grams of total salts per 1,000 grams of sea water (salinity .32 per cent. to .33 per cent.), and the following table gives the correction which McClendon found must be applied in order to find the true PH of sea water of any other salinity:

Salinity of Sea Water in Grams of Total Salts per 1,000 Grams of Water.	Correction to be Applied to the Reading of the Colorimetric Tube to Find the True PH of the Sea Water.
30	+ 0.02
31	+ 0.01
32-33	+ 0.
34	- 0.01
35	- 0.02
36	- 0.03
37	- 0.04

The carbon dioxide tension of the sea water was calculated from the true PH and the temperature according to the ratio determined experimentally by McClendon, 1917, p. 36. McClendon found that the PH of sea water normally declines .01 for 1° C. decline in temperature. Thus if the PH is 8.22 at 28° it may be expected to be 8.21 at 27° C. I find this to be true under normal conditions, but if the sea water is diluted with river water rich in CO₂ or mingled with large amounts of up-welling water from the depths, this relation may even be reversed. Thus in the Tropical Pacific I have observed a *rise* of 0.13 in the PH while the temperature sank 0.45° C. In general, however, under normal conditions, McClendon's rule holds good both for the Atlantic and the Pacific.

The salinity of the sea water is expressed in grams of total salts per 1,000 grams of water, and was determined by titration with AgNO₃, using K₂CrO₄ as indicator, and standard sea water obtained from Professor Martin Knudsen for comparison.

The thermometers read to $\frac{1}{10}^{\circ}$ C. and were compared with a thermometer standardized by the U. S. Bureau of Standards.

The currents were determined by the drift of the ship from her expected position. Naturally only a decided current could be detected by this crude method, but it was the only one available. The sea water was dipped up in a glass vessel from the stern of the vessel and tested at once for hydrogen-ion concentration and temperature, and a sample was preserved for determination of salinity. Experiments showed that no contamination from the ship could be detected if the water were dipped up from the stern rather than from the bow, waste from the sides of the ship being forced away from the stern by the back wave of the wake.

SUMMARY.

Through the simple process of placing a few drops of the red dye thymolsulphonephthalein in the bottom of a test tube and filling the tube with sea water we can determine its hydrogen-ion concentration. The more alkaline the water the more blue-green the color while relatively acid water gives a yellowish-green color.

In the Tropical Pacific the surface water drifting toward the

west is decidedly alkaline, about 8.23 PH, and its carbon dioxide tension is about 0.0003 atmospheres, and thus about in balance with the air. Back set currents moving in an easterly direction are, however, often encountered in the equatorial mid-Pacific especially in about 5° north latitude. This water is somewhat cooler than that of the prevailing westerly current, its carbon dioxide tension is decidedly acid, ranging from about 8.1 to 8.18 PH. Thus it comes from depths wherein the water is at least from 5° to 13° C. colder than the temperature of the surface of the ocean, and therefore from at least 100 to 200 fathoms beneath the surface (see chart No. 19, "Narrative of *Challenger* Expedition," Vol. 1, part 2, p. 758).

The gusty character of the trade winds combined with the general up-welling of deep water in the equatorial region may be a primary cause of this easterly current which consists of deep water that has come to the surface.

My conclusions support those of McClendon that the PH of sea water is dependent chiefly upon the temperature, and not upon the salinity of the water. A fall of 1° C. in temperature normally corresponds with a decline of about 0.01 in the PH as found by McClendon, but this may be altered by local conditions, such as dilution by relatively acid fresh water, or by the coming to the surface of cool deep water heavily charged with CO₂ which it discharges into the atmosphere upon being heated.

The cold shore current along the Atlantic coast of America between Nova Scotia and Florida is relatively acid in comparison with the Gulf Stream, being 7.9 to about 8.1 in winter, and its carbon dioxide tension is lower than that of the air, due possibly to photosynthesis maintained by its abundant plant life. It is thus absorbing carbon dioxide from the air. Thus the colder surface waters are absorbing carbon dioxide, while the tropical regions are probably setting it free into the atmosphere.

The detection of the sudden and marked change from blue-green to yellow-green when one encounters an easterly set in the Tropical Pacific, or passes from a warm into a cold current, can be so easily made that this method may prove of value in navigation.

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